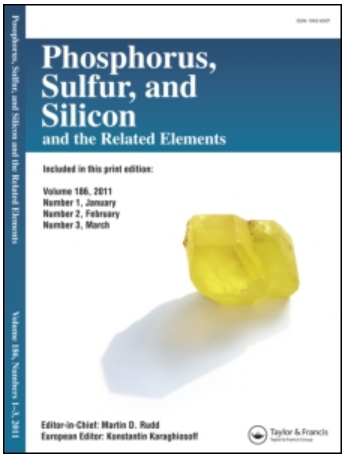

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SYNTHESIS OF β-TRIMETHYLARSONIUMLACTATE

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SHORT COMMUNICATION

SYNTHESIS OF β-TRIMETHYLARSONIUMLACTATE

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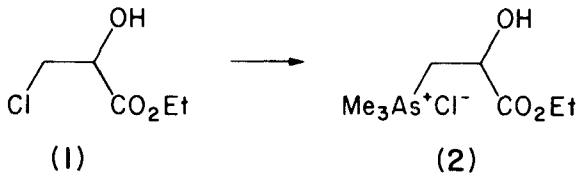
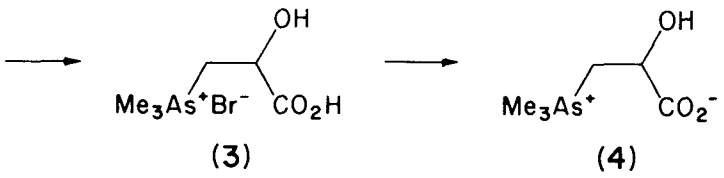
The biochemistry of arsenic is of considerable interest owing to the widespread presence of the element in marine organisms.[1] The substance arsenobetaine ($Me_3\overset{+}{As}CH_2\overset{-}{CO_2}$) has been isolated from the tail muscle of the western rock lobster (*Panulirus longipes cygnus*) and from the flesh of the dusky shark (*Carcharhinus obscurus*) and subsequently characterized by independent synthesis and X-ray crystal structure analysis.[2] In addition, two arsenic-containing ribose derivatives have been isolated from the brown kelp *Ecklonia radiata*, which is part of the coastal ecosystem to which the rock lobster belongs.[3] Assimilation, reduction, and methylation of arsenate also occurs in photosynthetic marine organisms,[4,5] particularly in phosphate-depleted tropical waters, and in molluscs and ascidians, where arsenic accumulation was found to be greatest in organisms bearing symbiotic algae.[5] Marine algae cultured in [^{74}As] arsenate synthesize an arsenic-containing phospholipid.[6] Base-catalysed deacylation of the lipid, followed by acid or enzyme hydrolysis of the intermediate phosphodiester, produced a product believed to be the β-trimethylarsoniumlactate, (**4**). However, a rigorous chemical characterization of the novel zwitterion was not undertaken. Accordingly, we describe here the synthesis of (**4**), together with some of its properties.





The most satisfactory route to (**4**) involves the quaternization of trimethylarsine with ethyl β-chlorolactate,[7] followed by saponification and deprotonation of the in-

termediate arsonium salts. The alternative procedure, based upon ring opening of potassium glycidate with trimethylarsine in ethanol, also gave (**4**), but in lower yield (ca. 15%), even after 100 h at 85°C.

The quaternization of trimethylarsine with (**1**) was carried out at 130°C in ethanol (12 days, sealed tube). The ester (**2**) was not isolated, but hydrolyzed with aqueous HBr(48%) to the arsonium acid bromide (**3**), which formed white prisms, mp 183°C (91% overall yield). Dowex 1 ion-exchange resin (200–400 mesh) in the hydroxide form deprotonated (**3**) to the desired product (**4**). Elution of the column with water, followed by evaporation of the eluate to dryness and recrystallization of the residue from ethanol/diethyl ether mixture gave the zwitterion as white plates, mp 199–201°C (92%). (Found: C, 34.7; H, 6.4; As, 35.7. Calcd for $C_6H_{13}AsO_3$: C, 34.6; H, 6.3; As, 36.0). ^{1}H NMR (MeOH-d_4): δ1.91 (s, 9, Me_3As^+), 2.75 (d, 2, *J*6Hz, CH_2), 4.24 (t, 1, *J*6Hz, CH). The resonances due to the ABX spin system were better resolved in the spectrum of the hydrobromide (**3**), *viz.*, δ1.95 (s, 9, Me_3As^+), 2.82 (q, 1, J_{AB}14Hz, J_{BX}8.5Hz, CH_AH_B), 2.97 (q, 1, J_{AB}14Hz, J_{AX}5Hz, CH_AH_B), 4.56 (dd, 1, J_{AX}5Hz, J_{BX}8.5Hz, CH). The ν (CO) vibration of (**4**) occurs at 1 600 cm^{-1} (compared to 1 740 cm^{-1} in the parent acid), which is similar to the value found for $Ph_3P^+CH_2CH_2CO_2^-$ (1 590 cm^{-1})[8] and characteristic of a carboxylate anion. Both (**3**) and (**4**) gave rise to identical methane chemical ionization spectra (200°C) showing the following pattern of ions: *m/z* 237 (8% RI, M + 29), 209 (100, MH^+), 163 (11, M—CO_2H), 121 (48, Me_3AsH^+), 105 (46), 103 (11). Under electron impact conditions (200°C/70 eV) the zwitterion (**4**) had the spectrum: *m/z* 179 (1%), 161 (2), 120 (80), 105 (90), 103 (100).

The present synthesis represents an extremely efficient and direct method of production of the zwitterion (**4**) from commercially available β-chlorolactic acid.[9] Moreover, should the corresponding optically active material be required, a method of resolution of β-chlorolactic acid is available.[10]

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